ROTATIONAL PARAMETERS FROM VIBRONIC EIGENFUNCTIONS OF JAHN-TELLER ACTIVE MOLECULES

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The structure in rotational spectra of many free radical molecules is complicated by Jahn-Teller distortions. Understanding the magnitudes of these distortions is vital to determining the equilibrium geometric structure and details of potential energy surfaces predicted from electronic structure calculations. For example, in the recently studied $\widetilde{A}^2E''$ state of the NO_3 radical, the magnitudes of distortions are yet to be well understood as results from experimental spectroscopic studies of its vibrational and rotational structure disagree with results from electronic structure calculations of the potential energy surface. By fitting either vibrationally resolved spectra or vibronic levels determined by a calculated potential energy surface, we obtain vibronic eigenfunctions for the system as linear combinations of basis functions from products of harmonic oscillators and the degenerate components of the electronic state. Using these vibronic eigenfunctions we are able to predict parameters in the rotational Hamiltonian such as the Watson Jahn-Teller distortion term, h_1, and compare with the results from the analysis of rotational experiments.